A STUDY OF THE CONDUCTIVITY OF CERTAIN ORGANIC ACIDS IN ABSOLUTE ETHYL ALCOHOL AT 15°, 25°, AND 35°.

BY

HOWARD HUNTLEY LLOYD.

DISSERTATION

Submitted to the Board of University Studies of
The Johns Hopkins University
at Baltimore
for the Degree of Doctor of Philosophy.
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CONTENTS.

Acknowledgment 4

Introduction 5

Historical 6

Experimental 18

Results 22

Measurements 23

Tables of Molecular Conductivity and of Temperature Coefficients of Conductivity 23

Tables of Changes in Concentration Due to Esterification.. 35

Figures 1 to 4 48-51

Discussion of the Results 52

Biographical Sketch 58

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I take this occasion to express my thanks to my co-worker, Mr. J. B. Wiesel, who aided me in carrying out the conductivity measurements, the results of which are herein recorded.

I owe a special debt of gratitude to my father, whose advice and assistance in the preparation of this work for publication were indispensable.

CONDUCTIVITY OF CERTAIN ORGANIC ACIDS IN ETHYL ALCOHOL.

INTRODUCTION

During the past six years a fairly thorough and systematic study of the conductivity and dissociation of aqueous solutions of organic acids, as affected by temperature as well as by dilution, has been in progress in this laboratory.[1] In view of the fact that very little work had been done upon solutions of organic acids in absolute ethyl alcohol, as will become evident from the historical review which follows, it was decided to extend our investigations into this field.[2] Accordingly, Wightman, Wiesel and Jones undertook a preliminary investigation of the problem, worked out a fairly satisfactory method of procedure and made conductivity measurements of nine organic acids.[3] The present investigation is a continuation and extension of their work.

1 Carnegie Inst. Wash. Pub. No. 170, Part II; No. 210, Chap. II.
2 Amer. Chem. Journ., 44, 156 (1910); 46, 56 (1911); 48, 320, 411 (1912); 50, 1 (1913).
3 Journ. Amer. Chem. Soc., 36, 2243 (1914). Carnegie Pub. No. 210, Chap. III.

HISTORICAL

The property of water, which, in the pure condition, conducts electricity only very slightly, to become conducting upon the addition of many compounds which of themselves are non-conducting, was known to de la Rive and was the subject of interesting experiments by Faraday; and the fact that solvents other than water exhibit the same phenomenon (of acquiring conductivity upon the addition of non-electrolytes) has been studied by a large number of workers;[4] but to Kohlrausch and Ostwald belongs the credit of having placed investigations in this field once and for all upon a firm scientific basis.

The contributions of Kohlrausch may be briefly described as follows: (1) the development of a convenient and precise method of measuring conductivity;[5] (2) the emphasis and the determination of the extent to which conductivity is influenced by temperature; (3) the reduction of conductivity measurements to definite, fixed units; (4) the reference of conductivity, not to weight per cent., as had been done previously, but to molecular volumes of solutions, that is, volumes which contain equivalent amounts of the dissolved substances;[6] (5) the enunciation of the law of the independent migration velocities of ions.

Ostwald made the conductivity method of Kohlrausch more complete and more practicable by reducing the apparatus and the manipulation to the simplest possible terms.[7] He also showed how the law of independent migration velocities of ions could be used to calculate the $\mu\infty$ values of organic acids from those of their sodium salts.[8] In addition, just after Arrhenius, on the basis of his dissociation theory, had pointed out[9] the necessity of the parallelism between the strengths of acids and their conductivities, it was Ostwald who, led to similar ideas by other considerations, succeeded in demonstrating[10] the existence of such a relation, and thereby made the first contribution to the application and significance of conductivity in questions of chemical affinity. Further, from thermodynamical considerations Ostwald derived his "dilution law,"[11] which permits the calculation,

4 Cf. Walden, Zeit. phys. Chem., 8, 433ff. (1891); 46, 103ff. (1903).
5 Pogg. Ann., 138, 379 (1869); 159, 233 (1876); Wied. Ann., 11, 653 (1880); 26, 161 (1885).
6 Wied. Ann., 6, 145 (1879).
7 Zeit. phys. Chem., 2, 561 (1888).
8 Ibid., 2, 270 (1888); 3, 170 (1889). Cf. also Amer. Chem. Journ. 46, 66 (1911).
9 Bih. t. k. Ak., 1884.
10 Journ. prak. Chem., 30, 93 (1884).
11 Zeit. phys. Chem., 2, 36, 270 (1888).

from the molecular conductivities of any weakly dissociated substance at different dilutions, of its affinity constant, which is independent of the degree of dilution and is conditioned only by the nature of the dissolved substance. During his classical investigations in this field[12] Ostwald determined the affinity constants of over 240 organic acids; and on the basis of these values drew many conclusions as to the composition and constitution of acids; thereby furnishing organic chemistry with a new and useful means of investigating questions of constitution.[13]

In a word, whereas Kohlrausch made the determination of conductivity possible, by establishing a convenient and accurate method of measuring it, Ostwald pointed out the practical importance of these measurements by indicating their bearing upon the solution of other chemical problems.

The first serious attempt to study the conductivity of alcoholic solutions of organic acids was made in 1888 by Hartwig.[14] This investigator employed the Kohlrausch method of measuring conductivity and worked with solutions of formic, acetic and butyric acids of varying concentrations at temperatures ranging from 0° to 30°. He found that conductivity increased with rise in temperature, and he calculated the temperature coefficients of conductivity by means of the equation

$$\kappa_t = \kappa_o (1 + \alpha t + \beta t^2).$$

No other conclusions, however, can be drawn from Hartwig's work, because he expressed his results in terms of grams of acid in 100 grams of solution, instead of in terms of molecular concentrations.

In 1889 Kablukoff[15] determined the conductivity of hydrochloric acid gas in absolute alcohol and in alcohol-water mixtures at 25°. He found the molecular conductivity in pure alcohol to be about one-sixteenth that in pure water. In the mixed solvent, the conductivity increases with increasing percentage of water, very slowly up to about twelve per cent. of water (by weight), and then more sharply. In every case the molecular conductivity increases slowly with dilution.

Wakeman,[16] in 1893, measured the conductivity of several organic acids and their sodium salts, as well as of hydrochloric acid, potassium iodide, potassium chloride and sodium chloride, in alco-

12 Zeit. phys. Chem., 3, 170, 241, 369 (1889).
13 Cf. also reference to work of Hantzsch and Voeglen, p. 12.
14 Wied. Ann [2], 33, 58 (1888).
15 Zeit. phys. Chem., 4, 429 (1889).
16 Zeit. phys. Chem., 11, 49 (1893).

hol-water mixtures ranging from pure water to fifty per cent. alcohol. Using Lenz's values[17] for the relative migration velocities of the potassium and iodine ions in solutions of potassium iodide, he was able, by means of his conductivity measurements, to calculate the relative migration velocities of the chlorine, hydrogen and sodium ions in the various mixed solvents which he employed. He then had all the data necessary to apply Ostwald's method[18] for the determination of the $\mu\infty$ values of the organic acids from those of their sodium salts. From these values it was a simple matter to calculate percentage dissociation, and thence, by means of Ostwald's dilution law, affinity constants.

The results obtained show that for a given acid at a given dilution, increase in the percentage of alcohol causes a slight decrease in dissociation and a more rapid decrease in the affinity constant (κ). For a definite alcohol-water mixture the value of κ decreases regularly with dilution, which seems to point to the action of an unknown influence which decreases the dissociation to such an extent that the formula $\frac{\alpha^2}{(1-\alpha)\nu}$ no longer holds. A very interesting feature of Wakeman's work is his attempt to extrapolate the value of molecular conductivity beyond 50 per cent. alcohol in the direction of 100 per cent. alcohol, and he postulates that the conductivity approaches zero as a limit.

Schall,[19] in 1894, determined the conductivity of oxalic, picric and dichloracetic acids in alcohol and in alcohol-water mixtures. The molecular conductivity of these acids in water is approximately the same, but Schall found that replacement of the water by alcohol decreases the conductivity to quite different extents. This he attributes chiefly to change in the degree of dissociation. In alcohol-water mixtures the acids were found to behave very differently from what they did in the pure solvents. Some appear to behave just the opposite of what might be expected: for example, picric acid gives a much higher, and each of the other acids a much lower conductivity value in water-alcohol mixtures than in pure alcohol.

In the meantime the conductivity method had been applied to solutions of electrolytes in a variety of non-aqueous solvents, with the result that not a single case was on record in which the Ostwald dilution law could be said to apply, even approximately. In order to test the validity of this law for alcoholic solutions,

17 Mem. de l'Acad. de St. Petersb., VII series, 30, 9 (1882).
18 Zeit. phys. Chem., 2, 270 (1888); 3, 170 (1889). See also Amer. Chem. Journ. 46, 66 (1911).
19 Zeit. phys. Chem., 14, 701 (1894).

Wildermann, in 1894, carried out an investigation[20] on the conductivity of certain organic acids (acetic, monochloracetic, dichloracetic, trichloracetic and succinic), in absolute alcohol at 18°. Absolute alcohol was obtained free from aldehyde by treatment with silver nitrate, and from water by heating with lime. Great care was exercised in protecting it from the air, and a special apparatus was constructed, with the aid of which a measured quantity could be drawn out of the supply bottle directly into the conductivity cells. Because of the small values of the conductivities to be measured the cells were constructed so as to have small constants; but in spite of this the external resistances required were high, and hence a graphite resistance rheostat was employed to make the tone minima more distinct. Before being used, the cells were washed with running water for 8 to 10 days. They could not be dried in the ordinary way by washing with alcohol and then evaporating the alcohol, because it was found that the alcohol which was in contact with the platinized electrodes was to some extent oxidized by the air to acetic acid. Therefore, after being washed with water, the cells were allowed to drain completely, after which alcohol was introduced so as to wash the glass walls without coming in contact with the electrodes, and then the alcohol was allowed to cover the electrodes. Some of the alcohol was then drawn off and fresh alcohol added, keeping the electrodes continuously covered, and this process repeated until the conductivity remained constant. This often cost a half-day of work and from 300 to 500 c. c. of good absolute alcohol. All the solutions were made up in the cell; the most concentrated by introducing approximately the desired quantity of acid, and from this the others by repeated replacement of a portion of the solution with fresh alcohol. The strength of each solution was determined by titration of the portion removed.

Wildermann found that the conductivity of acetic, monochloracetic and succinic acids was so small that the values were unreliable, and he was content to make the qualitative statement that between the volumes 10 and 160 these substances have a molecular conductivity which increases almost directly proportional to the volume.

In order to understand fully his conclusions in regard to the stronger acids, it will be necessary to consider briefly a few mathematical relations which Wildermann deduced from the dilution law of Ostwald.

As Ostwald showed,[21] the dilution law— $\frac{\mu\infty\ (\mu\infty - \mu_v)\ v}{\mu^2{}_v} = \kappa$..(I)

20 Zeit. phys. Chem., 14, 231 (1894).
21 Zeit. phys. Chem., 2, 270 (1888).

takes the form..... $\mu^2_v = \nu\kappa$ .....(II)
for weakly dissociated compounds. Assuming that a given acid in alcoholic solution obeys the dilution law, if we increase the volume from (ν) to(ν_1), we have, instead of (I) and (II)

$$\frac{\mu\infty\ (\mu\infty - \mu_{v1})\ \nu_1}{\mu^2_{v1}} = \kappa \text{ .....(I').}$$

and .....$\mu^2_{v1} = \nu\kappa^1$ .....(II')
Combining (II) and (II') we get

$$\frac{\mu^2_{v1}}{\mu^2_v} = \frac{\nu_1}{\nu} \text{ or } \frac{\mu_{v1}}{\mu_v} = \sqrt{\frac{\nu_1}{\nu}}$$

Likewise, from (I) and (I') there results

$$\frac{\mu^2_{v1}}{\mu^2_v} = \frac{\mu\infty - \mu_{v1}}{\mu\infty - \mu_v}\ \frac{\nu_1}{\nu}$$

Since $\nu_1 > \nu$, $\mu_{v1} > \mu_v$ and therefore—

$$\frac{\mu\infty - \mu_{v1}}{\mu\infty - \mu_v} < 1$$

it follows that $\frac{\mu^2_{v1}}{\mu^2_v}$ is always less than $\frac{\nu_1}{\nu}$ and approaches this value as a limit. Therefore, as molecular conductivity increases in concentrated solutions, as long as the compound is slightly dissociated the values of $\frac{\mu^2_{v1}}{\mu_v}$ found experimentally will not differ greatly from $\frac{\nu_1}{\nu}$ but with increasing dilution and greater degree of dissociation $\frac{\mu^2_{v1}}{\mu^2_v}$ will decrease in value and differ more and more from $\frac{\nu_1}{\nu}$.

As a result of his conductivity measurements on di- and trichloracetic and β-resorcylic acids, Wildermann drew the following conclusions:

"(1) For dichloracetic acid, when $\nu < 10$ liters the value of $\frac{\mu_{v1}}{\mu_v}$ is less than $\sqrt{\frac{\nu_1}{\nu}}$; above 10 liters, $\frac{\mu_{v1}}{\mu_v}$ is greater than $\sqrt{\frac{\nu_1}{\nu}}$ at dilutions from 800 to 2000 liters $\frac{\mu_{v1}}{\mu_v}$ becomes almost equal to

$\frac{v_1}{v}$. The increase of $\frac{\mu_{v1}}{\mu_v}$ is, therefore, continuous, not only in concentrated solutions but also in the more dilute, to which the equation—

$$\frac{\mu\infty\ (\mu\infty - \mu_v)\ v}{\mu^2_v} = \kappa$$

should apply."

"(2) The same conclusions are even more nearly true in the case of β-resorcylic acid, where the increase of $\frac{\mu_{v1}}{\mu_v}$ is almost proportional to the volume."

(3) In the case of trichloracetic acid, with increase in dilution from 20 to 300 liters $\frac{\mu_{v1}}{\mu_v}$ approaches $\sqrt{\frac{v_1}{v}}$, and beyond 300 liters a relation obtains which can be expressed approximately by the dilution law. The fact that the values of $\frac{\mu_{v1}}{\mu_v}$ for solutions more concentrated than 300 liters are not in keeping with the dilution law was confirmed in a later investigation[22] by Wildermann using an independent method. An explanation of this anomalous condition was offered in a previous paper[23] and will not be discussed here.

(4) It had been pointed out by Ostwald, that in aqueous solutions the degree of dissociation of the same dilution of trichloracetic, dichloracetic, monochloracetic, and acetic acids showed a decrease in the order named. A like succession was observed by Wildermann for the same acids in alcohol.

In summing up, Wildermann says that it is possible to apply the Kohlrausch method to the determination of the conductivity of strong organic and inorganic acids in alcoholic solution, but that reliable results could not be obtained for such weak acids as acetic, monochloracetic. and succinic. However, even in the cases where the method is best applicable, much time and patience on the part of the experimenter are required to obtain results that are at all dependable.

Because of the difficulty which he experienced in applying the Kohlrausch method to the study of the conductivity of weakly dissociated organic acids in absolute alcohol as a solvent, Wildermann employed another method[24] for the investigation of these

22 Zeit. phys. Chem., 14, 247 (1894).
23 Ber., 26, 1782 (1893).
24 Zeit. phys. Chem., 14, 247 (1894).

acids. This consists in the use of a direct current of high voltage (140-150 volts). Polarization can be neglected, and since the external resistances are large, the measurement of conductivity resolves itself into the measure of the strength of the current. This is done comparatively by means of a reflecting galvanometer, the solutions being contained in capillary tubes of varying lengths and diameters. The same conclusions were reached as before, except that the galvanometer method was found susceptible of more general application than that of Kohlrausch.

This method has been found open to objection by Malmström,[25] who prefers a method described by Nernst[26] whenever small conductivities are to be measured.

In 1902 Hantzsch and Voegelen[27] found the conductivity method capable of distinguishing between a true acid and a so-called "pseudo-acid," which in aqueous solution partly breaks down into the constituent ions of the true acid. The application of the method in this instance depends upon the different behavior of the molecular conductivities of true and pseudo-acids in aqueous-alcoholic solutions containing different percentages of alcohol. If it is desired to test whether a given hydrogen compound is a pseudo-acid or not, a true acid with approximately the same affinity constant is selected, and the molecular conductivity of both determined in aqueous alcohol at a given dilution. Then, without varying the dilution, the percentage of alcohol is increased and the resulting conductivities determined. If the molecular conductivity of the hydrogen compound decreases much more slowly than that of the true acid, it is a pseudo-acid. Hantzsch and Voegelen offered no explanation for this difference in behavior, but they supported their discovery with widely different examples.

In the last few years Heinrich Goldschmidt[28] has applied the conductivity method to alcoholic solutions of organic acids, in order to determine the equilibrium hydrogen ion-alcohol-water; and he has succeeded in throwing new light on the mechanism of esterification and on the formation of complex ions.

In his earlier work (1895) on the kinetics of esterification in alcoholic solutions of organic acids, Goldschmidt had observed that the catalytic action of strong acids in accelerating esterification was greatly diminished by the addition of water. He ex-

25 Zeit. phys. Chem., 22, 331 (1897).
26 Zeit. phys. Chem., 14, 622 (1894).
27 Ber., 35, 1001 (1902).
28 Zeit. Elektroch., 15, 4 (1909); Zeit. phys. Chem., 70, 627 (1910); Ibid., 81, 30 (1912); Zeit. Elektroch., 20, 473 (1914); Zeit. phys. Chem., 89, 129 (1914).

plained this on the assumption that the accelerating action of a strong acid was due to the formation of a complex molecule by union of the acid with alcohol, and that the retardation was brought about by the decomposition of this molecule by water. For example, if hydrochloric acid were acting as the catalyser, a compound C_2H_5OH, HCl would be formed, and this would be acted upon by water according to the equation—

$$C_2H_5OH, HCl + H_2O \rightleftarrows C_2H_5OH + H_2O, HCl. \qquad (I)$$

For a time[29] Goldschmidt thought that only the ionized portion of the complex molecule took part in the esterification, and he undertook to determine from measurements of reaction velocity the equilibrium in the reaction—

$$(C_2H_5OH,H^+) + H_2O = C_2H_5OH + (H_2O,H^+). \qquad (II)$$

He found that a number of organic acids which were esterified in the presence of hydrochloric acid showed the same retardation when equal volumes of water were added. From this he concluded that his assumption was correct and he calculated the equilibrium constant (ρ) for the equilibrium—

$$\rho = \frac{(C_2H_5OH,H^+) \times H_2O}{(H_2O,H^+)}$$

to be 0.15.

Later (1909) Goldschmidt noticed that when weaker acids, such as trichlorbutyric, picric, etc., were used as accelerators, the effect of water upon the reaction velocity could not be calculated by means of the constant $\rho = 0.15$, but that a much smaller value had to be selected. Under these conditions not only the ionized part of the double compound alcohol-acid was acting as catalyser (according to equation II), but also the undissociated portion (as represented in equation I). Consequently the constant 0.15 was not wholly dependent upon the relation between the ions, and could not be used to characterize the equilibrium hydrogen ion-alcohol-water. Goldschmidt, therefore, devised a new way of obtaining this equilibrium constant, namely, the determination of the limiting conductivities of acids in absolute and aqueous alcoholic solutions.

The molecular conductivity of an acid in absolute alcohol at infinite dilution is expressed by the well-known equation—

$$\mu_o = v + \nu \qquad (I)$$

where v equals the migration velocity of the cations and ν that of the anion. (It is assumed that there are at least two kinds of cations in the solution—free hydrogen ions and complex ions (C_2H_5OH,H^+) ; but since the ratio of these two must always be constant they may be considered as one). As soon as water is added, a new kind of ion is formed—(H_2O,H^+). If the concentra-

29 Zeit. phys. Chem., 60, 728 (1907).

tion of the water added be η moles per liter, and the migration velocity of the ions (H_2O,H^+) be v^1, the conductivity at infinite dilution, $\mu\eta$, will be expressed by the equation—

$$\mu\eta = \chi v + (1 - \chi)\, v_1 + \nu \qquad \text{(II)}.$$

where χ represents the fraction of a gram cation which is still present in the original condition (as free or alcoholated hydrogen ion), and $1 - \chi$ the fraction transformed into the hydrated ion—(H_2O,H^+). Therefore, the equilibrium equation, which expresses the distribution of hydrogen ions between alcohol and water, is—

$$\frac{\chi\eta}{1 - \chi} = \rho^{30}$$

whence $$\chi = \frac{\rho}{\eta + \rho} \text{ and } 1 - \chi = \frac{\eta}{\eta + \rho}$$

Substituting these values in (II), we have—

$$\mu\eta = \frac{\rho}{\eta + \rho}\, v + \frac{\eta}{\eta + \rho}\, v^1 + \nu$$

and, since $\nu = \mu_o - v$ this reduces to—

$$(\mu_o - \mu\eta)\,(\eta + \rho) = (v - v^1)\,\eta \qquad \text{(III)}.$$

If we know μ_o and the values of $\mu\eta$ corresponding to two or more values of η, the equation can be solved for ρ, the equilibrium constant, and for $v - v^1$, the difference between the migration velocity of the cations in anhydrous alcohol and that of the hydrated ion—(H_2O,H^+) in aqueous alsohol. Therefore, in order to test the equation, it is only necessary to determine the conductivity at infinite dilution of several organic acids in pure alcohol and in two or more alcohol-water mixtures.

The greatest experimental difficulty in doing this lay in the preparation of pure absolute alcohol. At first[31] metallic calcium was used for this purpose (von Winkler's method), but the alcohol prepared in this way, although practically free from water, was found[32] to contain considerable amounts of ammonia (formed by the action of water upon the calcium nitride present in the calcium); and hence this method had to be abandoned. After further experimentation a satisfactory product was finally obtained in the following manner: Ordinary 95 per cent. alcohol was allowed to stand in contact with lime for some time and then distilled (Kailan). This treatment reduced the water content to about 0.006—normal, or 0.12 gram per liter. The same process was repeated, this time using a distilling vessel and condenser of copper; and the amount of water present was decreased to 0.003—normal, or 0.06 gram per liter. If a completely anhydrous alcohol

30 Zeit. phys. Chem., 89, 134 (1914)
31 Zeit. Elektroch., 15, 4 (1909).
32 Zeit. phys. Chem., 81, 30 (1912).

was desired, the product of the first distillation was treated with calcium. For this purpose calcium bars were turned on a lathe to remove the coating of hydroxide, and the bright metal was cut into pieces the size of a pea. An amount of calcium equal to ten times the amount of water present (about 0.1 gram) was introduced into the alcohol. The whole was then heated for several hours, with a reflux condenser attached, and a rapid stream of dry air was passed through the distillation chamber to remove traces of ammonia. In this way absolute alcohol was obtained having a specific conductivity of 2×10^{-7}.

With a good quality of alcohol in his possession Goldschmidt was ready to test his equation, and he began his study with hydrochloric acid. First, the molecular conductivity in absolute alcohol was measured, at dilutions ranging from 10 to 5120 liters; and from the values obtained for the more dilute solutions μo, the conductivity at infinite dilution, was calculated with the aid of Kohlrausch's formula—

$$\mu\infty = \mu_v + \alpha \sqrt[3]{\frac{1}{\nu}}$$

The mean value of μ_o proved to be 89. Then the conductivity in aqueous alcohol containing different amounts of water (η) was determined over the same range of dilution, and the limiting conductivity, $\mu\eta$, corresponding to each alcohol-water mixture, was estimated as before. The results show that the molecular conductivity of solutions of hydrochloric acid in alcohol first decreases with increasing percentage of water, then passes through a minimum at $\eta = 2$, and finally begins to increase again. $\mu\infty$ behaves in a similar manner.

Using the value 89 for μ_o, and combining with it the values of $\mu\eta$ obtained for the different water concentrations (η), Goldschmidt solved equation (III) for ρ and $v - v^1$, and obtained the constants 0.0583 and 42.7 respectively. (The high value of $v - v^1$ shows that the complex ion (H_2O,H^+) travels much more slowly than the free or the alcoholated hydrogen ion). The constancy of ρ and $v - v^1$ is evidenced in favor of the correctness of the reasoning by which the equation was developed.

In order to determine the limit of applicability of the constants 0.0583 and 42.7, Goldschmidt used these constants to recalculate the values of $\mu\eta$. He found satisfactory agreement between the calculated values and those obtained experimentally, so long as the percentage of water (η) in the alcohol did not exceed unity. (Beyond this point there was a lack of agreement, caused no doubt by the influence of water upon the migration velocities of the ions). Thus, Goldschmidt showed that by means of the

constants 0.0583 and 42.7 the effect of water on the conductivity of alcoholic solutions of strong acids could be calculated.

Desiring to adduce further evidence in support of his theory, Goldschmidt took up a study of the conductivity of sulphosalicylic acid. He found the behavior of this acid entirely analogous to that of hydrochloric. The molecular conductivity in alcohol was influenced to the same extent by the addition of water; and the amount of this influence could be calculated with the aid of the constants 0.0583 and 42.7. The limiting conductivity in absolute alcohol, μ_o, was estimated both from the $\mu\infty$ value of the sodium salt (by the method of Ostwald) and from the $\mu\infty$ values of the free acid in aqueous alcohol (by means of equation III); and the figure obtained was the same (83) in both cases.

Satisfied with the results of his investigations upon the stronger acids, Goldschmidt next turned his attention to the weaker—picric, trichloracetic, trinitrobenzoic, trichlorbutyric, dichloracetic and salicylic. He observed that in every case the molecular conductivity increased with increase in the concentration of the water present in the solution. The $\mu\infty$ values for the weaker acids could not be determined directly, as had been done previously for the strong acids, and Goldschmidt employed the method of Ostwald for calculating the limiting conductivity of an acid from that of its sodium salt. The values obtained are given in the following table:

Acid.	$\mu\infty$ (Na salt)	$\mu\infty$ (acid)
Hydrochloric	47	89
Sulphosalicylic	41	83
Picric	51	93
Trichloracetic	46	88
Trinitrobenzoic	44	86
Trichlorbutyric	45	87
Dichloracetic	48	90
Salicylic	44	86

A glance at this table reveals the fact that the difference in the migration velocities of the anions is very slight.

From the $\mu\infty$ values of the acids the degrees of dissociation (α) and the affinity constant κ were calculated. The following values of κ were obtained for the solutions in absolute alcohol:

Acid	κ
Picric	1.8×10^{-4}
Trichloracetic	1.5×10^{-6}
Trinitrobenzoic	8.3×10^{-7}
Trichlorbutyric	1.0×10^{-7}
Dichloracetic	7.2×10^{-8}
Salicylic	2.4×10^{-9}

The influence of water upon the values of κ was also investigated, with the result that κ was found to increase regularly with increasing concentration of water. The law of this increase was expressed in the form of an equation which Goldschmidt deduced from theoretical considerations.

In conclusion, Goldschmidt showed that the influence of the weaker acids upon the velocity of esterification could be calculated by means of the constant 0.0583. The calculated values agreed very satisfactorily with those obtained experimentally.

This work of Goldschmidt's has been discussed at some length, not because it is a final word on the subject with which it deals, but for the reason that it presents an excellent illustration of the ever-increasing applicability of the conductivity method to the solution of chemical problems.

EXPERIMENTAL

Reagents.

The alcohol used in this investigation was prepared in the following way: Ordinary 95 per cent. alcohol was heated for several days with lime in a copper tank provided with a ground-brass stopper and reflux condenser, and then distilled through a block-tin condenser. The product of this distillation was reheated with fresh lime and again distilled, the first and last portions of the distillate being discarded. The receiver for the distillate was a 6-liter Jena glass bottle having a three-holed paraffined cork as stopper. Through one hole passed a siphon, through another an adapter with a glass stopcock, and through the third a calcium chloride-soda lime tube. In this way the alcohol was well protected, during distillation, from impurities in the air, and small quantities sufficient for making up the solutions could be drawn off without exposing the main supply. By exercising extreme care it is possible by this method to obtain alcohol having a specific gravity of 0.78506 to within the limit of error + 0.00002. According to Circular 19 of the Bureau of Standards such alcohol is pure. The alcohol employed in the conductivity measurements varied in specific gravity from 0.78506 to 0.78517, the latter containing 99.964 per cent. alcohol.

The organic acids were obtained from Kahlbaum and Schuchardt. The same methods of purifying them were employed as when the conductivities of these acids were determined in aqueous solution.[33] After purification they were carefully dried in a vacuum dessicator containing sulphuric acid. Whenever practicable the melting-points of the acids were taken as one criterion of purity.

Aqueous solutions of ammonia were used for titration purposes, since ammonia had been found by Wightman, Wiesel and Jones[34] to give the most satisfactory results. These solutions were prepared as follows: Concentrated ammonia was heated and the gas which was given off was passed first over sodium hydroxide, which collected a large part of the water-vapor and any carbon dioxide; then over sodium, which absorbed the remainder of the water-

33 Amer. Chem. Journ., 44, 156 (1910); 46, 56 (1911); 48, 320, 411 (1912); 50, 1 (1913).

34 Journ. Amer. Chem. Soc., 36, 2247-9 (1914).

vapor; and finally into a weighed quantity of conductivity water in a measuring flask, until the amount necessary to make a 0.1 N solution was dissolved. By diluting this solution with conductivity water any desired strength of ammonia could be obtained. The normality of each solution employed was determined by titration against standard sulphuric acid.

Corallin (rosolic acid) was used as the indicator, because it is sensitive to ammonia and to organic acids and is not sensitive to carbon dioxide except when the latter is present in fairly large quantity. The end-point with corallin is not quite as sharp and distinct as with phenolphthalein, and considerable practice is necessary before reliable results can be obtained.

Apparatus.

On account of the high resistance of the alcoholic solutions of the acids it was found necessary to make use entirely of the cylindrical type of conductivity cell. The method of obtaining the constants of these cells was described by White[35] and by Wightman.[36]

Since the percentage temperature coefficients of conductivity for substances dissolved in alcohol, as well as the coefficient of expansion of the alcohol itself, are so large, it is necessary to regulate the temperature as closely as possible. This was done by the combination of a specially devised gas regulator and thermo-regulator. These have already been described in a paper by Davis and Hughes.[37]

The constant-temperature baths were of the improved form designed by Davis,[38] of this laboratory. These baths are of about 60 liters capacity and are made of copper. Heat is applied to a heavy iron pipe outside the bath and water is kept circulating through this pipe by means of propellers. Only a small portion of the water in the thermostat comes into immediate contact with the heated surface, and this portion is subsequently mixed with the main body of water, thereby securing much more even distribution of temperature. In these baths ordinarily the temperature does not vary more than 0.02°, which is sufficiently constant for our purpose. With greater precautions as to insulation against changes in temperature, and with further modification of the thermo-regulator, the variation can be decreased to a few thousandths of a degree.

35 Amer. Chem. Journ., 42, 527 (1909).
36 Ibid., 44, 64 (1911).
37 Zeit. phys. Chem., 85, 519 (1913).
38 Carnegie Inst. Wash. Pub. No. 210, p. 121 (1914).

A 1/12 horse-power direct-current motor served as a source of power for the stirrers, the power being transmitted by belt drives. The motor proved to be a great improvement over the hot-air engines formerly used.

The thermometers were of the differential Beckman type and were carefully compared with a standard Reichsanstalt thermometer, which had been calibrated also at the United States Bureau of Standards.

The resistance box which was used throughout this entire investigation had also been calibrated at the Bureau of Standards. A very fine Kohlrausch slide-wire bridge was employed, by means of which it was possible to read distances on the slide-wire corresponding to tenths of a millimeter (the total length of the wire was 5 meters).

Flasks, pipettes, and burettes for measuring purposes were in all cases carefully calibrated.

Procedure.

The solutions of the organic acids in alcohol were made up in 200 c. c. Jena measuring flasks calibrated for 25°. The quantity of dried and purified acid necessary to make a solution of the required normality was weighed out on a watch glass and was washed off through a funnel into one of the measuring flasks. The flask was shaken until all the acid had dissolved; it was then filled to the neck with alcohol and suspended in the 25° bath. When temperature equilibrium was reached it was filled to the mark. In the meantime a conductivity cell was thoroughly washed with pure alcohol and dried with filtered dry air. It was then nearly filled with the solution which had been made up and placed in the 15° bath. The measuring flask containing the remainder of the solution was returned to the 25° bath. In this way four dilutions of each acid were prepared—N/8, N/32, N/128 and N/512; and the four cells containing them placed in the 15° bath. In addition, a fifth cell was employed to measure the conductivity of the pure solvent.

After the cells had remained in the 15° bath for at least an hour the conductivities of the solutions were measured. Titrations of the acids against the standard ammonia were made simultaneously with the conductivity measurements. For this purpose 10 c. c. of the solution in question were removed by means of a pipette from the proper measuring flask in the 25° bath. A second titration in each case served to confirm the results of the first.

When the conductivities of the four solutions and of the alcohol had been determined at 15°, the cells were removed to the 25°

bath; and after the lapse of an hour measurements were made as before. The same procedure was followed for the determinations at 35°.

At first thought it would seem probable that keeping the solutions in the flasks at a constant temperature (25°), and subjecting the solutions in the cells to changes in temperature (15° to 35°), would produce a change in the rates of esterification. If this were true, the normalities of the solutions in the cells would be different from the values obtained by the titration of the solutions in the flasks, and a considerable error would be introduced. It was found, however, that there was no appreciable difference in the amount of acid present at any moment in a given solution, whether the solution was kept in the 25° bath continuously for 8 hours or whether it was transferred from one bath to another during this time. The reason for this is no doubt to be found in the extremely slow rate at which, under the conditions of this investigation, esterification takes place.

Although it is fairly certain, then, that variation in the temperature has no measurable effect upon the rate of esterification in alcoholic solutions of the organic acids, this variation does alter, to a considerable extent, the volume, and therefore, the concentration, of these solutions. For example, a solution which has a volume of 1000 c. c. at 25°, contracts to 989.23 c. c. when cooled to 15°, and expands to 1011.14 c. c. when warmed to 35°. Because of this fact a correction has to be applied to the volume calculated from titration, before molecular conductivity can be estimated at 15° and 35°. This correction was made in the following way: Let us suppose that the normality of a given solution at 25, as determined by titration against ammonia, is N_{25}. The normality at 15°, N_{15}, would then be expressed by the ratio $\frac{N_{25}}{.98923}$; and the true volume at 15° (i. e., the number of liters which contain a gram molecular weight of the dissolved acid) would be the reciprocal of this ratio, or $\frac{.98923.}{N_{25}}$ Similarly, the normality at 35° would be $\frac{N_{25}}{1.01114}$ and the volume would be $\frac{1.01114.}{N_{25}}$

RESULTS

In the following tables of conductivity results, Vm is the volume at which the solutions were made up; Vc is the corrected volume. The corrections were applied in the manner just described, both for expansion or contraction of the alcohol, and for change in the concentration of the acid due to formation of ester. Molecular conductivity μ_v was calculated in the usual manner.

A word of explanation should be added in regard to the method of calculating temperature coefficients of conductivity. The formulæ generally employed in the determination of these coefficients are $T = \frac{\mu_{t^1} - \mu_t}{t^1 - t}$ and $\Delta = \frac{T}{\mu_t}$, where μ_t and μ_{t^1} represent the molecular conductivities of the same solution at t and t^1, respectively, ($t^1 > t$), T is the temperature coefficient expressed in conductivity units, and Δ is the percentage temperature coefficient. But these formulæ as such are not applicable to alcoholic solutions of organic acids because the true volume (Vc) of a given solution is different at different temperatures (due to the causes already described). For example, in the case of benzoic acid (see Table I), the N/8 solution was found to have a volume of 7.945 at 15°, of 8.05 at 25°, and of 8.15 at 35°. Before the conductivities of these three solutions can be compared they must be reduced to values corresponding to the same volume. For the sake of simplicity Vc at 25° is taken as the standard of reference. The reduction of μ_v at 15° to Vc at 25° is made in the following way: The specific conductivity at 15° ($\frac{0.002892}{7.945} = 0.000364$) is multiplied by the difference in volume at 15° and 25° (8.05 — 7.945 = 0.105). The product (0.000038) is added to the molecular conductivity at 15° (0.002892), giving 0.002930, which represents the molecular conductivity at 15° of a solution of volume 8.05. This value (0.002930) and the value of μ_v at 25° (0.004073) can then be substituted for μ_v and μ_{t^1} in the above equations, and T and Δ are found to be 0.0001143 and 3.90 respectively. Similarly, the specific conductivity at 35° ($\frac{0.005444}{8.15} = 0.000668$) is multiplied by the difference in volume at 25° and 35° (8.15 — 8.05 = 0.10). The product (0.000067) is subtracted from the molecular conductivity at 35° (0.005444), giving 0.005377, which represents the molecular conductivity at 35° of a solution of volume 8.05. This value (0.005377) and the value of μ_v at 25° (0.004073) can then be substituted for μ_{t^1} and μ_t in the formulæ and T and Δ are determined to be 0.0001304 and 3.20 respectively.

MEASUREMENTS

Tables of Molecular Conductivity and of Temperature Coefficients of Conductivity.

TABLE I.—Benzoic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.945	0.002892	8.05	0.004073	8.15	0.005444
32	32.62	0.009884	32.99	0.01405	33.51	0.01893
128	137.3	0.04311	143.3	0.06205	149.7	0.08563
512	536.7	0.1583	544.7	0.2233	552.2	0.2960

Specific conductivity of alcohol at 15°, 0.000168; at 25°, 0.000149; at 35°, 0.000125.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.001143	3.90	0.001304	3.20
32	0.00405	4.05	0.00459	3.27
128	0.01715	3.82	0.01992	3.21
512	0.0626	3.90	0.0687	3.08

TABLE II.—Phenylacetic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.94	0.004176	8.04	0.005660	8.13	0.007325
32	32.70	0.01122	33.42	0.01614	34.08	0.02167
128	146.9	0.04392	152.2	0.06347	156.9	0.08598
512	537.9	0.1581	545.0	0.2245	552.2	0.2976

Specific conductivity of alcohol at 15°, 0.000168; at 25°, 0.000149; at 35°, 0.000125.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.001431	3.38	0.001584	2.80
32	0.00467	4.07	0.00510	3.16
128	0.01797	3.95	0.01993	3.14
512	0.0643	4.01	0.0692	3.08

TABLE III.—Mandelic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	8.10	0.005370	8.20	0.007273	8.30	0.009553
32	32.60	0.01232	33.01	0.01680	33.57	0.02216
128	129.2	0.03256	130.8	0.04303	132.6	0.05529
512	455.2	0.09377	498.0	0.1389	504.8	0.1787

Specific conductivity of alcohol at 15°, 0.000050; at 25°, 0.000054; at 35°, 0.000056.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.001837	3.38	0.002165	2.98
32	0.00412	3.30	0.00499	2.97
128	0.00989	2.98	0.01151	2.65
512	0.0361	3.51	0.0374	2.69

TABLE IV.—Cinnamic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.97	0.001370	8.06	0.001782	8.16	0.002350
32	32.81	0.003612	33.28	0.004603	33.85	0.006222
128	141.6	0.01297	144.0	0.01660	146.9	0.02205
512	535.1	0.04243	541.4	0.04737	548.3	0.06585

Specific conductivity of alcohol at 15°, 0.000070; at 25°, 0.000084; at 35°, 0.000092.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.000397	2.87	0.000539	3.02
32	0.000939	2.56	0.001514	3.29
128	0.00341	2.58	0.00501	3.02
512	0.00444		0.01763	3.72

TABLE V.—Phenylpropiolic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.95	0.01797	8.04	0.02240	8.13	0.02712
32	32.23	0.03400	32.61	0.04278	32.99	0.05181
128	135.3	0.06868	137.5	0.08641	139.8	0.1070
512	532.4	0.1535	538.8	0.1932	545.1	0.2478

Specific conductivity of alcohol at 15°, 0.000070; at 25°, 0.000084; at 35°, 0.000092.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.00423	2.32	0.00442	1.97
32	0.00838	2.44	0.00843	1.97
128	0.01661	2.39	0.01883	2.18
512	0.0379	2.44	0.0519	2.69

TABLE VI.—Mesaconic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	8.11	0.006683	8.22	0.008393	8.36	0.01044
32	31.67	0.01264	32.47	0.01636	33.16	0.02059
128	130.5	0.03132	132.6	0.04005	134.6	0.05074
512	551.1	0.1080	564.3	0.1405	575.5	0.1784

Specific conductivity of alcohol at 15°, 0.000067; at 25°, 0.000071; at 35°, 0.000074.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.001619	2.39	0.00187	2.23
32	0.00340	2.62	0.00380	2.32
128	0.00823	2.59	0.00994	2.48
512	0.0299	2.70	0.0351	2.50

TABLE VII.—Maleic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.95	0.1504	8.04	0.1922	8.14	0.2400
32	32.24	0.2913	32.86	0.3768	33.38	0.4736
128	136.3	0.5977	139.8	0.7806	145.1	1.0034
512	532.7	1.184	540.5	1.537	546.8	1.932

Specific conductivity of alcohol at 15°, 0.000078; at 25°, 0.000074; at 35°, 0.000071.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.0401	2.64	0.0449	2.34
32	0.0799	2.69	0.0894	2.37
128	0.1676	2.73	0.1862	2.38
512	0.336	2.80	0.373	2.43

TABLE VIII.—Fumaric Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.98	0.00471	8.09	0.00629	8.19	0.00815
32	32.66	0.00941	33.20	0.01291	33.79	0.01710
128	140.3	0.0282	144.8	0.0392	145.8	0.0515
512	535.0	0.0920	543.2	0.1276	550.4	0.1668

Specific conductivity of alcohol at 15°, 0.000078; at 25°, 0.000074; at 35°, 0.000071.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per. cent.	Cond. units.	Per cent.
8	0.00152	3.19	0.00176	2.80
32	0.00334	3.49	0.00389	3.01
128	0.0110	3.78	0.0119	3.04
512	0.0342	3.66	0.0370	2.90

TABLE IX.—Itaconic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.95	0.01452	8.05	0.01946	8.14	0.02504
32	32.25	0.05870	32.74	0.07795	33.20	0.09963
128	133.0	0.2413	135.6	0.3214	137.9	0.4100
512	532.1	0.9737	538.5	1.2762	545.1	1.531

Specific conductivity of alcohol at 15°, 0.000471; at 25°, 0.000391; at 35°, 0.000314.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.00476	3.24	0.00530	2.72
32	0.01836	3.08	0.02030	2.60
128	0.0754	3.06	0.0818	2.54
512	0.2908	2.95	0.2360	1.85

TABLE X.—Aconitic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.95	0.01359	8.045	0.01757	8.15	0.02238
32	33.06	0.02529	33.63	0.03403	34.26	0.04481
128	150.1	0.06649	155.6	0.09492	164.2	0.1309
512	539.1	0.1838	545.2	0.2606	551.9	0.3471

Specific conductivity of alcohol at 15°, 0.000159; at 25°, 0.000139; at 35°, 0.000117.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.00382	2.78	0.00452	2.57
32	0.00830	3.24	0.00996	2.93
128	0.02599	3.77	0.0292	3.08
512	0.0747	4.02	0.0823	3.16

TABLE XI.—o-Toluic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.98	0.005429	8.08	0.006721	8.17	0.008174
32	32.63	0.01299	33.07	0.01637	33.48	0.01992
128	140.0	0.04298	142.7	0.05680	144.7	0.06917
512	537.3	0.1230	543.5	0.1745	549.8	0.2078

Specific conductivity of alcohol at 15°, 0.000090; at 25°, 0.000102; at 35°, 0.000113.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.001228	2.24	0.001357	2.02
32	0.00320	2.43	0.00331	2.02
128	0.01299	2.96	0.01141	2.01
512	0.0501	4.03	0.0309	1.77

TABLE XII.—p-Toluic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.95	0.001288	8.04	0.001648	8.13	0.002163
32	32.27	0.003453	32.68	0.004444	33.09	0.005923
128	136.0	0.01387	138.3	0.01770	141.4	0.02588
512	532.7	0.04262	539.1	0.05283	545.7	0.06930

Specific conductivity of alcohol at 15°, 0.000070; at 25°, 0.000084; at 35°, 0.000092.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.000345	2.65	0.000491	2.98
32	0.000947	2.71	0.001406	3.16
128	0.00360	2.55	0.00761	4.30
512	0.00970	2.25	0.01563	2.96

TABLE XIII.—Benzilic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.96	0.01660	8.05	0.02200	8.14	0.02799
32	32.17	0.05527	32.56	0.07267	33.04	0.09271
128	134.0	0.2176	137.1	0.2882	141.0	0.3711
512	531.8	0.8849	537.9		544.8	1.217

Specific conductivity of alcohol at 15°, 0.000441; at 25°, 0.000379; at 35°, 0.000320.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.00521	3.10	0.00568	2.58
32	0.01673	2.99	0.01869	2.57
128	0.0656	2.95	0.0726	2.52
512	0.260	2.90		

TABLE XIV.—Oxyisobutyric Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.99	0.005234	8.08	0.006666	8.17	0.008346
32	32.71	0.01429	33.33	0.01813	33.84	0.02264
128	139.5	0.05022	143.3	0.06391	147.3	0.07969
512	537.6	0.1699	543.8	0.2208	550.1	0.2718

Specific conductivity of alcohol at 15°, 0.000092; at 25°, 0.000107; at 35°, 0.000120.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.001374	2.58	0.001584	2.38
32	0.00357	2.45	0.00417	2.30
128	0.01232	2.39	0.01383	2.16
512	0.0489	2.84	0.0479	2.17

TABLE XV.—Malonic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	8.12	0.0190	8.13	0.0237	8.18	0.0319
32	32.9	0.0434	33.2	0.0555	33.7	0.0737
128	129.3	0.0775	129.5	0.0985	129.6	0.1351
512	512.8	0.2533	514.9	0.3160	518.1	0.4338

Specific conductivity of alcohol at 15°, 0.000254 to 0.000246; at 25°, 0.000257 to 0.000249.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.0046	2.45	0.0079	3.39
32	0.0113	2.67	0.0192	3.59
128	0.0207	2.61	0.0359	3.69
512	0.0613	2.42	0.1145	3.64

TABLE XVI.—Ethylmalonic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.96	0.01937	8.05	0.02590	8.15	0.03346
32	32.28	0.06333	32.70	0.08345	33.13	0.1066
128	134.9	0.2459	137.1	0.3236	140.6	0.4134
512	532.4	0.9924	538.5	1.295	545.1	1.624

Specific conductivity of alcohol at 15°, 0.000441; at 25°, 0.000379; at 35°, 0.000320.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.00631	3.22	0.00715	2.76
32	0.01930	3.01	0.02175	2.60
128	0.0727	2.91	0.0795	2.46
512	0.291	2.90	0.309	2.39

TABLE XVII.—Propylmalonic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.95	0.03271	8.04	0.04220	8.13	0.05280
32	32.21	0.07995	32.63	0.1049	33.09	0.1326
128	136.0	0.2739	139.1	0.3663	141.4	0.4628
512	533.3	1.021	539.4	1.346	545.7	1.692

Specific conductivity of alcohol at 15°, 0.000471; at 25°, 0.000391; at 35°, 0.000314.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.00912	2.76	0.01002	2.37
32	0.0239	2.95	0.0259	2.47
128	0.0862	3.08	0.0890	2.43
512	0.313	3.03	0.326	2.42

TABLE XVIII.—Butylmalonic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.97	0.0169	8.08	0.0219	8.19	0.0277
32	32.89	0.0269	33.65	0.0363	34.26	0.0479
128	142.3	0.0549	147.8	0.0794	153.2	0.1069
512	535.0	0.1257	547.6	0.1780	555.0	0.2364

Specific conductivity of alcohol at 15°, 0.000078; at 25°, 0.000075; at 35°, 0.000071.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.0048	2.82	0.0054	2.47
32	0.0088	3.20	0.0108	2.97
128	0.0224	3.93	0.0237	2.98
512	0.0493	3.83	0.0553	3.10

TABLE XIX.—Benzylmalonic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.95	0.03391	8.04	0.04200	8.13	0.05155
32	32.23	0.04880	32.64	0.06189	33.04	0.07738
128	134.7	0.1043	137.1	0.1361	139.4	0.1723
512	533.0	0.3017	539.1	0.4032	545.7	0.5091

Specific conductivity of alcohol at 15°, 0.000149; at 25°, 0.000137; at 35°, 0.000125.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.00771	2.25	0.00898	2.14
32	0.01167	2.36	0.01455	2.35
128	0.0299	2.81	0.0334	2.45
512	0.0980	3.21	0.0997	2.47

TABLE XX.—Allylmalonic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.97	0.01309	8.06	0.01757	8.15	0.02304
32	33.07	0.02867	33.52	0.03882	34.01	0.05068
128	142.4	0.08701	145.2	0.1170	148.6	0.1491
512	540.6	0.2822	546.7	0.3756	553.4	0.4798

Specific conductivity of alcohol at 15°, 0.000149; at 25°, 0.000137; at 35°, 0.000125.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.00433	3.27	0.00522	2.97
32	0.00976	3.36	0.01108	2.85
128	0.0283	3.19	0.0286	2.44
512	0.0902	3.16	0.0984	2.62

TABLE XXI.—Diethylmalonic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.95	0.02857	8.05	0.03860	8.14	0.05022
32	32.25	0.06042	32.66	0.08044	33.04	0.1054
128	136.0	0.1257	139.1	0.1732	142.2	0.2279
512	533.3	0.2527	539.4	0.3441	546.0	0.4494

Specific conductivity of alcohol at 15°, 0.000066; at 25°,0.000077; at 35°, 0.000088.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.00967	3.34	0.01107	2.87
32	0.01845	3.01	0.02376	2.95
128	0.0446	3.47	0.0497	2.87
512	0.0885	3.46	0.0999	2.90

TABLE XXII.—Dipropylmalonic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	8.12	0.03354	8.22	0.04453	8.33	0.05772
32	31.29	0.06759	31.84	0.09058	32.45	0.1178
128	130.3	0.1416	131.9	0.1889	133.6	0.2442
512	540.3	0.3031	548.8	0.4078	558.3	

Specific conductivity of alcohol at 15°, 0.000067; at 25°, 0.000071; at 35°, 0.000074.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.001619	2.39	0.00187	2.23
32	0.00340	2.62	0.00380	2.32
128	0.00823	2.59	0.00994	2.48
512	0.0299	2.70	0.0351	2.50

TABLE XXIII.—m-Chlorbenzoic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.94		8.04	0.005422	8.15	0.007153
32	32.84	0.01136	33.40	0.01610	33.79	0.02149
128	147.8	0.04907	151.7	0.06978	157.4	0.09523
512	537.9	0.1829	545.0	0.2556	552.2	0.3402

Specific conductivity of alcohol at 15°, 0.000159; at 25°, 0.000139; at 35°, 0.000117.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8			0.001641	3.03
32	0.00455	3.94	0.00514	3.19
128	0.01942	3.86	0.02200	3.15
512	0.0707	3.81	0.0802	3.14

TABLE XXIV.—m-Nitrobenzoic Acid.

Molecular Conductivity.

Vm.	Vc.	μ_v 15°	Vc.	μ_v 25°	Vc.	μ_v 35°
8	7.98	0.005725	8.08	0.007470	8.17	0.009575
32	32.65	0.01786	33.07	0.02308	33.54	0.02915
128	140.8	0.07293	143.5	0.09414	146.9	0.1178
512	537.9	0.2754	544.1	0.3526	550.7	0.4362

Specific conductivity of alcohol at 15°, 0.000133; at 25°, 0.000139; at 35°, 0.000145.

Temperature Coefficients of Conductivity.

	15°-25°		25°-35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.001680	2.90	0.001995	2.67
32	0.00522	2.89	0.00566	2.45
128	0.01981	2.66	0.0210	2.23
512	0.0740	2.66	0.0784	2.22

Tables of Changes in Concentration Due to Esterification.

The rate at which the organic acids combine with alcohol can be seen from the following data. "Time in minutes" represents the time which elapsed between the preparation and the titration of the solution in question. "Per cent. decrease in normality," estimated by dividing the difference between the calculated normality and the observed normality by the calculated normality, shows the rate of ester formation. In anticipation of the discussion to follow, it should be said that too much confidence ought not to be placed in the absolute values of per cent. decrease. The relative values of these figures, however, are thoroughly reliable, and lead to interesting conclusions, as will be pointed out later.

TABLE XXV.—Benzoic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
180	0.1245	0.1250	0.40
350	0.1242	0.1250	0.64
440	0.1240	0.1250	0.80
185	0.03033	0.03125	2.94
360	0.03031	0.03125	3.01
450	0.03017	0.03125	3.46
185	0.007204	0.007812	7.78
360	0.006979	0.007812	10.66
450	0.006753	0.007812	13.56
190	0.001843	0.001953	5.63
370	0.001836	0.001953	5.99
450	0.001831	0.001953	6.25

TABLE XXVI.—Phenylacetic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
170	0.1246	0.1250	0.32
380	0.1244	0.1250	0.48
460	0.1243	0.1250	0.56
180	0.03025	0.03125	3.20
390	0.02992	0.03125	4.26
465	0.02967	0.03125	5.06
180	0.006733	0.007812	13.81
390	0.006570	0.007812	15.90
465	0.006446	0.007812	17.48
190	0.001839	0.001953	5.84
400	0.001835	0.001953	6.04
470	0.001831	0.001953	6.25

TABLE XXVII.—Mandelic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
155	0.1221	0.1250	2.32
320	0.1219	0.1250	2.48
445	0.1218	0.1250	2.56
165	0.03031	0.03125	3.01
325	0.03029	0.03125	3.07
445	0.03012	0.03125	3.62
175	0.007655	0.007812	2.01
340	0.007647	0.007812	2.11
445	0.007627	0.007812	2.37
180	0.002173	0.001953	
345	0.002008	0.001953	
445	0.002003	0.001953	

TABLE XXVIII.—Cinnamic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
185	0.1242	0.1250	0.66
375	0.1241	0.1250	0.72
475	0.1239	0.1250	0.88
200	0.03015	0.03125	3.52
390	0.03005	0.03125	3.84
480	0.02987	0.03125	4.42
110	0.006987	0.007812	10.56
300	0.006946	0.007812	11.08
390	0.006885	0.007812	11.87
120	0.001849	0.001953	5.33
300	0.001847	0.001953	5.43
390	0.001844	0.001953	5.58

TABLE XXIX.—Phenylpropiolic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
145	0.12446	0.12500	0.43
325	0.12444	0.12500	0.45
420	0.12436	0.12500	0.51
160	0.03069	0.03125	1.79
335	0.03067	0.03125	1.86
430	0.03065	0.03125	1.92
225	0.007314	0.007812	6.37
395	0.007273	0.007812	6.90
490	0.007232	0.007812	7.42
255	0.001858	0.001953	4.86
400	0.001856	0.001953	4.97
500	0.001855	0.001953	5.02

TABLE XXX.—Mesaconic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
175	0.1220	0.1250	2.40
385	0.1217	0.1250	2.64
480	0.1210	0.1250	3.20
185	0.03122	0.03125	0.12
395	0.03080	0.03125	1.77
480	0.03049	0.03125	2.99
195	0.007579	0.007812	2.98
395	0.007539	0.007812	3.50
480	0.007512	0.007812	3.84
210	0.001795	0.001953	8.09
405	0.001772	0.001953	9.27
490	0.001757	0.001953	10.03

TABLE XXXI—Maleic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
180	0.1245	0.1250	0.40
350	0.1243	0.1250	0.54
450	0.1242	0.1250	0.64
190	0.03068	0.03125	1.82
360	0.03043	0.03125	2.61
450	0.03029	0.03125	3.07
190	0.007256	0.007812	7.12
355	0.007153	0.007812	8.44
445	0.006970	0.007812	10.78
195	0.001857	0.001953	4.92
360	0.001850	0.001953	5.27
450	0.001849	0.001953	5.33

TABLE XXXII.—Fumaric Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
180	0.1239	0.1250	0.88
350	0.1237	0.1250	1.06
460	0.1235	0.1250	1.22
180	0.03029	0.03125	3.07
355	0.03012	0.03125	3.62
465	0.02992	0.03125	4.26
185	0.007051	0.007812	9.74
360	0.006909	0.007812	11.56
470	0.006786	0.007812	13.13
195	0.001849	0.001953	5.33
375	0.001841	0.001953	5.74
475	0.001837	0.001953	5.94

TABLE XXXIII.—Itaconic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
195	0.1244	0.1250	0.49
345	0.1243	0.1250	0.56
445	0.1242	0.1250	0.63
200	0.03067	0.03125	1.86
350	0.03054	0.03125	2.27
445	0.3046	0.03125	2.53
160	0.007437	0.007812	4.80
310	0.007375	0.007812	5.59
410	0.007334	0.007812	6.12
170	0.001859	0.001953	4.81
315	0.001857	0.001953	4.92
415	0.001855	0.001953	5.02

TABLE XXXIV.—Aconitic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
180	0.1244	0.1250	0.48
340	0.1243	0.1250	0.56
460	0.1241	0.1250	0.72
185	0.02992	0.003125	4.26
345	0.02974	0.003125	4.83
460	0.02951	0.003125	5.57
190	0.006590	0.007812	15.64
350	0.006426	0.007812	17.74
460	0.006160	0.007812	21.15
200	0.001835	0.001953	6.04
360	0.001834	0.001953	6.09
470	0.001832	0.001953	6.19

TABLE XXXV.—o-Toluic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
170	0.1239	0.1250	0.88
350	0,1238	0.1250	0.96
455	0.1237	0.1250	1.04
180	0.03032	0.03125	2.98
360	0.03024	0.03125	3.23
465	0.03020	0.03125	3.36
180	0.007068	0.007812	9.52
365	0.007007	0.007812	10.30
465	0.006988	0.007812	10.55
185	0.001841	0.001953	5.73
370	0.001840	0.001953	5.79
470	0.001839	0.001953	5.84

TABLE XXXVI.—p-Toluic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
195	0.1244	0.1250	0.48
365	0.12438	0.1250	0.50
475	0.1243	0.1250	0.56
215	0.03065	0.03125	1.92
375	0.03060	0.03125	2.08
480	0.03056	0.03125	2.21
195	0.007273	0.007812	6.90
345	0.007232	0.007812	7.42
455	0.007151	0.007812	8.46
200	0.001857	0.001953	4.92
355	0.001855	0.001953	5.02
465	0.001853	0.001953	5.12

TABLE XXXVII.—Benzilic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
180	0.12432	0.12500	0.54
345	0.12426	0.12500	0.59
520	0.12417	0.12500	0.66
190	0.03075	0.03125	1.60
355	0.03071	0.03125	1.73
525	0.03060	0.03125	2.08
165	0.007380	0.007812	5.53
330	0.007294	0.007812	6.63
500	0.007171	0.007812	8.20
170	0.001860	0.001953	4.76
335	0.001859	0.001953	4.81
505	0.001856	0.001953	4.97

TABLE XXXVIII.—Oxyisobutryic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
175	0.1238	0.1250	0.96
335	0.12377	0.1250	0.98
440	0.1237	0.1250	1.04
180	0.03024	0.03125	3.23
340	0.03000	0.03125	4.00
445	0.02988	0.03125	4.38
185	0.007091	0.007812	9.23
345	0.006980	0.007812	10.65
445	0.006866	0.007812	12.11
200	0.001840	0.001953	5.79
350	0.001839	0.001953	5.84
455	0.001838	0.001953	5.89

TABLE XXXIX.—Malonic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
220	0.1232	0.1250	1.44
330	0.1229	0.1250	1.68
420	0.1222	0.1250	2.24
230	0.03039	0.03125	2.75
330	0.03008	0.03125	3.75
430	0.02966	0.03125	5.09
180	0.00773	0.00781	1.05
330	0.00772	0.00781	1.18
420	0.00771	0.00781	1.31
190	0.001950	0.001953	0.16
340	0.001942	0.001953	0.51
430	0.001930	0.001953	1.18

TABLE XL.—Ethylmalonic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
190	0.12425	0.12500	0.60
340	0.12419	0.12500	0.65
450	0.12411	0.12500	0.71
190	0.03065	0.03125	1.92
340	0.03058	0.03125	2.14
455	0.03052	0.03125	2.34
160	0.007334	0.007812	6.12
305	0.007294	0.007812	6.63
425	0.007191	0.007812	7.95
165	0.001858	0.001953	4.86
310	0.001857	0.001953	4.92
430	0.001855	0.001953	5.02

TABLE XLI.—Propylmalonic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
150	0.1244	0.1250	0.48
325	0.12436	0.1250	0.51
435	0.12428	0.1250	0.58
155	0.03071	0.03125	1.73
330	0.03065	0.03125	1.92
435	0.03056	0.03125	2.21
100	0.007273	0.007812	6.90
270	0.007191	0.007812	7.95
365	0.007151	0.007812	8.46
100	0.001855	0.001953	5.02
270	0.001854	0.001953	5.07
365	0.001853	0.001953	5.12

TABLE XLII.—Butylmalonic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
175	0.1241	0.1250	0.69
345	0.1238	0.1250	0.96
440	0.1235	0.1250	1.20
185	0.03008	0.03125	3.72
355	0.02972	0.03125	4.90
445	0.02952	0.03125	5.55
185	0.006950	0.007812	11.03
355	0.006766	0.007812	13.39
445	0.006602	0.007812	15.49
195	0.001849	0.001953	5.33
360	0.001826	0.001953	6.50
450	0.001822	0.001953	6.71

TABLE XLIII.—Benzylmalonic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
195	0.1245	0.1250	0.40
355	0.1244	0.1250	0.48
460	0.1243	0.1250	0.56
195	0.03069	0.03125	1.79
355	0.03064	0.03125	1.95
465	0.03060	0.03125	2.08
165	0.007345	0.007812	5.98
325	0.007294	0.007812	6.63
435	0.007253	0.007812	7.16
165	0.001856	0.001953	4.97
320	0.001855	0.001953	5.02
430	0.001853	0.001953	5.12

TABLE XLIV.—Allylmalonic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
145	0.12413	0.12500	0.70
335	0.12407	0.12500	0.74
455	0.12403	0.12500	0.78
155	0.02991	0.03125	4.29
345	0.02983	0.03125	4.54
460	0.02973	0.03125	4.86
125	0.006946	0.007812	9.80
315	0.006885	0.007812	11.87
425	0.006803	0.007812	12.92
135	0.001830	0.001953	6.30
325	0.001829	0.001953	6.35
435	0.001827	0.001953	6.45

TABLE XLV.—Diethylmalonic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
200	0.12440	0.12500	0.48
360	0.12425	0.12500	0.60
465	0.12415	0.12500	0.68
210	0.03067	0.03125	1.86
370	0.03062	0.03125	2.02
475	0.03060	0.03125	2.08
165	0.007273	0.007812	6.90
330	0.007191	0.007812	7.95
485	0.007110	0.007812	8.99
165	0.001855	0.001953	5.02
330	0.001854	0.001953	5.07
485	0.001852	0.001953	5.17

TABLE XLVI.—Dipropylmalonic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
195	0.1218	0.1250	2.56
360	0.1216	0.1250	2.72
465	0.1214	0.1250	2.88
205	0.03162	0.03125	....
365	0.03141	0.03125	....
470	0.03116	0.03125	....
225	0.007595	0.007812	2.78
375	0.007580	0.007812	2.97
480	0.007566	0.007812	3.15
230	0.001831	0.001953	6.25
395	0.001822	0.001953	6.71
485	0.001811	0.001953	7.27

TABLE XLVII.—m-Chlorbenzoic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
160	0.1245	0.1250	0.40
355	0.1243	0.1250	0.56
470	0.1241	01.250	0.72
170	0.03012	0.03125	3.62
365	0.02994	0.03125	4.19
480	0.02992	0.03125	4.26
175	0.006692	0.007812	14.34
375	0.006590	0.007812	15.64
480	0.006426	0.007812	17.74
185	0.001839	0.001953	5.84
375	0.001835	0.001953	6.04
480	0.001831	0.001953	6.25

TABLE XLVIII.—m-Nitrobenzoic Acid.

Time in minutes.	Observed normality.	Calculated normality	Per cent. decrease in normality.
160	0.12389	0.12500	0.89
340	0.12383	0.12500	0.94
455	0.12376	0.12500	0.99
165	0.03030	0.03125	3.04
345	0.03024	0.03125	3.23
455	0.03015	0.03125	3.52
175	0.007028	0.007812	10.04
355	0.006967	0.007812	10.78
465	0.006885	0.007812	11.87
180	0.001839	0.001953	5.84
360	0.001838	0.001953	5.89
465	0.001836	0.001953	5.99

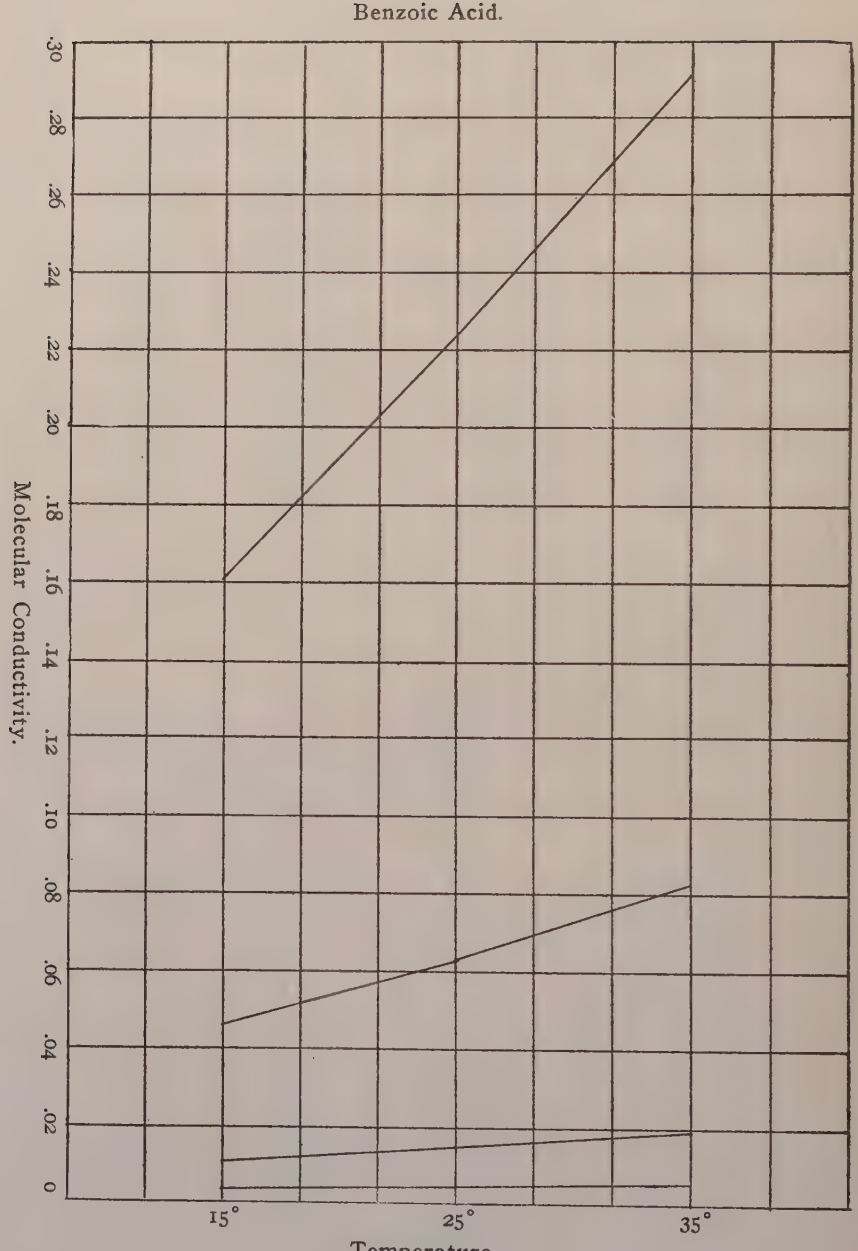

Benzoic Acid.
Molecular Conductivity.
.30
.28
.26
.24
.22
.20
.18
.16
.14
.12
.10
.08
.06
.04
.02
0
15°
25°
35°
Temperature.

Figure 1.

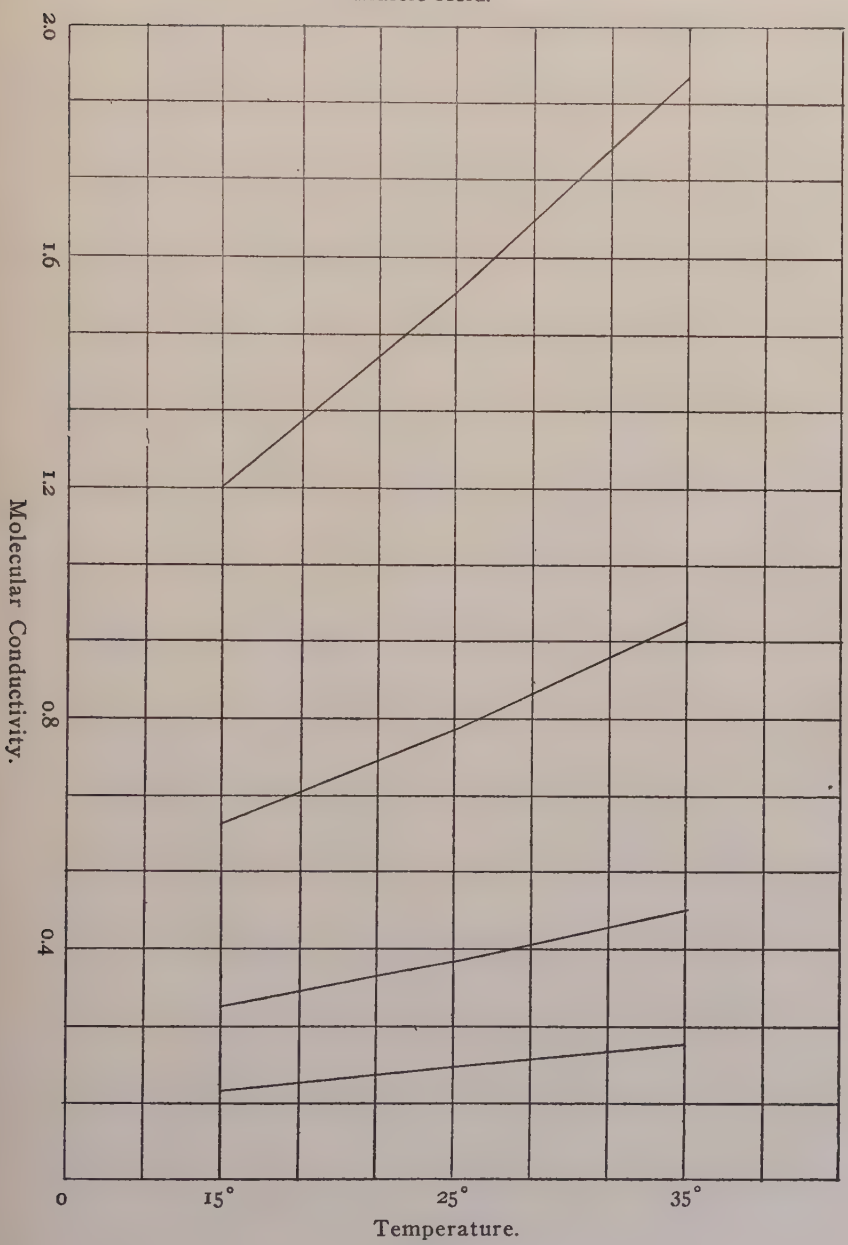

Maleic Acid.
2.0
1.6
1.2
0.8
0.4
Molecular Conductivity.
0
15°
25°
35°
Temperature.

Figure 2.

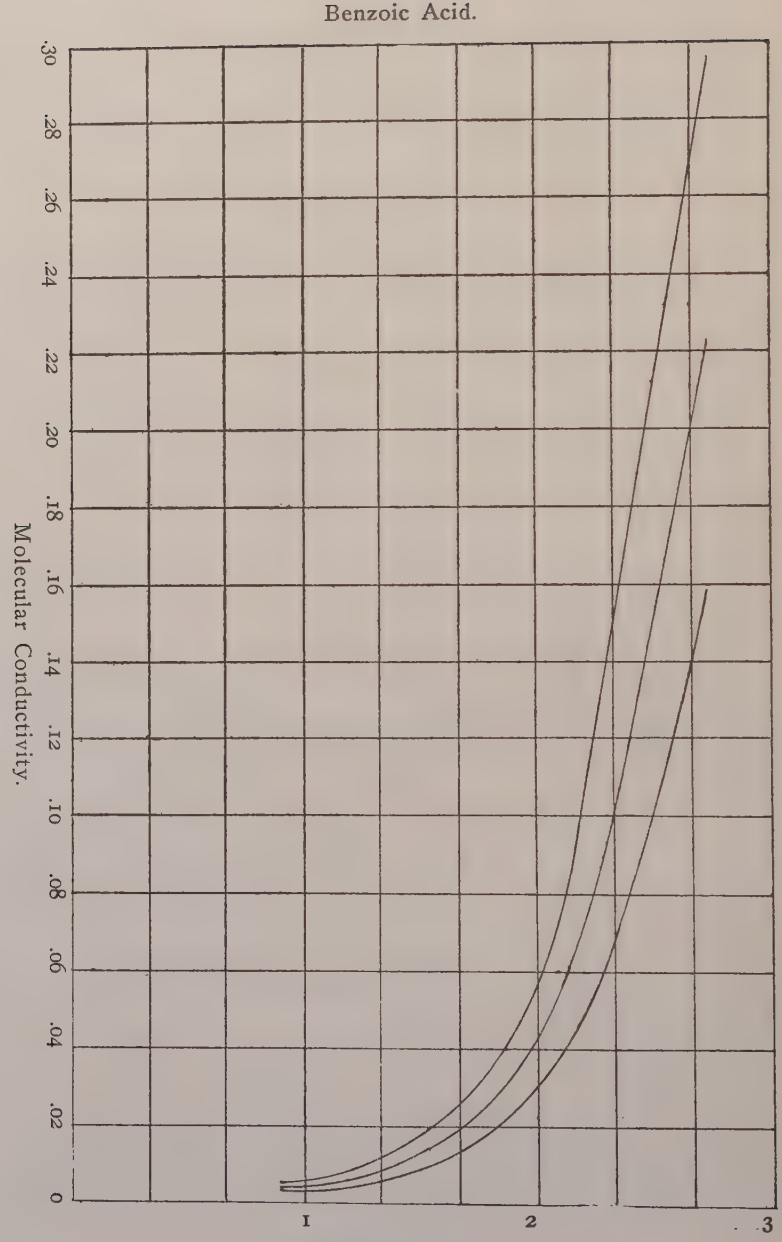

Benzoic Acid.
.30
.28
.26
.24
.22
.20
.18
.16
.14
.12
.10
.08
.06
.04
.02
0
Molecular Conductivity.
1
2
3
Log. Volume.

Figure 3.

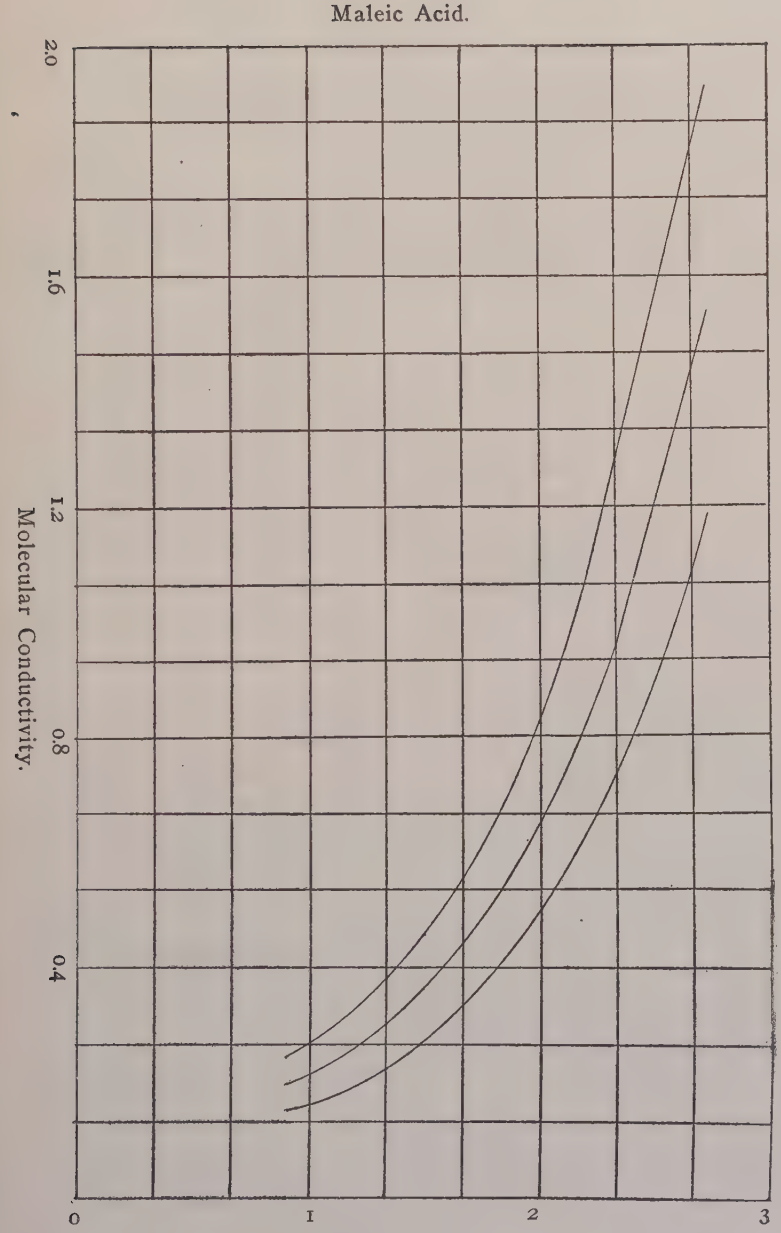

Maleic Acid.
2.0
1.6
1.2
0.8
0.4
Molecular Conductivity.
0
1
2
3
Log. Volume.

Figure 4.

DISCUSSION OF RESULTS

The most striking feature of the conductivities of the organic acids in alcohol, as shown by an examination of the foregoing tables, is their extremely small value. It will be recalled that Wakeman,[39] in the course of his work on alcohol-water mixtures, plotted curves of conductivity of the organic acids against percentage alcohol; and, on extending the curves in the direction of 100 per cent. alcohol, found that they apparently approached zero conductivity as a limit. As can be seen from my results, the conductivities do not actually approach zero, but they never exceed 2, and in the great majority of cases fall below unity. It will also be remembered that because of the extremely high resistances offered by alcoholic solutions of the organic acids, Wildermann[40] abandoned the Kohlrausch method as a means of studying the conductivities of these solutions. The difficulty which he experienced was obviated by the author by the use of cells with much smaller constants than those he employed. Even with this improvement, it was found necessary to discard all the very weak organic acids, such as the members of the acetic acid series.

The conductivities of the organic acids in alcohol are several hundred times smaller than the conductivities of the same acids in water. When we consider the fact that alcohol has from one-fourth to one-fifth the dissociating power of water, as shown by the dissociation of strong electrolytes in these solvents, the above fact does not at present seem to admit of any very satisfactory explanation.

The percentage temperature coefficients of conductivity vary from 2.5 to 4 per cent. and decrease with rise in temperature. They are uniformly higher than the corresponding values in aqueous solutions, which range from 1 to 2.5 per cent. In the light of the work that has been done in this laboratory, these results suggest the following possibilities:

(1) It might be that there is greater alcoholation in alcoholic solutions than hydration in aqueous solutions, and that the amount of alcoholation decreases with rise in temperature. This view, however, is not substantiated by previous experiences. The alcoholates may be more unstable with rise in temperature than

39 Cf. p. 8.
40 Cf. p. 12.

the hydrates, but alcohol seems to have in general far less power to combine with dissolved substances than water.

(2) If the temperature coefficient of fluidity of alcohol were greater than that of water with rise in temperature, the ions in alcoholic solutions would have greater freedom of movement than in aqueous solutions. This would account for the larger temperature coefficients of conductivity in alcoholic solutions. Unfortunately, such is not the case. The temperature coefficient of fluidity of water is greater than that of alcohol, as can be seen from the following values calculated from the results of Wightman, Davis, Holmes, and Jones:[41]

TABLE XLVIX.

Fluidities.

	15°	25°	35°
Water	88.18	112.23	138.89
Alcohol	77.45	94.88	114.80

Temperature Coefficients of Fluidity.

	15°-25°	25°-35°
Water	2.73	2.37
Alcohol	2.25	2.10

Nevertheless, it is possible that the greater expansion of alcohol with rise in temperature affords the ions greater freedom of movement.

(3) A suggestion which seems to be far more probable than either of the two preceding, is that the association of alcohol is affected to a less extent by rise in temperature than is the association of water. If this be true, the dissociating power of alcohol relative to that of water will become greater with rise in temperature. This would explain the greater temperature coefficients of conductivity of alcoholic solutions.

The increase in conductivity with rise in temperature can be seen from Figs. 1 and 2. The curves have very much the appearance of those for aqueous solutions. This suggests the thought that perhaps the increase of molecular conductivity in alcohol with rise in temperature is, as in aqueous solutions, a parabolic function and that the Euler equation—

$$\mu_v = \mu_o + at - bt^2$$

applies to both. This will be tested in later work by determining the conductivities of some of the acids at temperatures other than

41 Journ. Chim. Phys., 12, 406 (1914).

15°, 25°, and 35°; and comparing the results obtained with those calculated from the above equation.

The effect of increase in dilution is to increase the molecular conductivity. The increase in conductivity in many cases is almost proportional to the volume. This relation is shown graphically in Figs. 3 and 4.

A knowledge of the extent to which organic acids are dissociated in alcoholic solution would be highly desirable. It is hoped that a method for the determination of percentage dissociation will be worked out here in the near future. It will be recalled that Goldschmidt[42] obtained values for the limiting conductivities of several organic acids in alcohol from the $\mu\infty$ values of their sodium salts. These varied from 83 to 93, depending on the nature of the acid. It has not yet been found practicable to determine the limiting conductivities of the organic acids studied in this investigation, but as a result of Goldschmidt's work it is certain that they do not differ greatly from 90. If this be the case, the dissociation of the organic acids studied by the author, as determined by conductivity, do not in any case exceed 2 per cent. even in N/512 solutions.

Relation Between Composition and Conductivity.

In his classical study of the conductivity of aqueous solutions of organic acids, to which reference has already been made,[43] Ostwald pointed out a number of relations between composition and molecular conductivity. The validity of these relations has been confirmed by the work which has been in progress in this laboratory for the past fifteen years. In view of this, an examination of the results obtained for alcoholic solutions in the attempt to discover similar relations should prove to be interesting.

Take first the series—

Phenylpropionic acid....$C_6H_5 — CH_2 — CH_2 — COOH$
Cinnamic acid.....$C_6H_5 — CH = CH — COOH$
Phenylpropiolic acid .....$C_6H_5 — C \equiv C — COOH$

The conductivity of phenylpropionic acid[44] is about twice that of cinnamic acid (Table IV). The removal of two hydrogen atoms with formation of a double bond thus decreases the conductivity. This is found to be true also in the case of propylmalonic and allylmalonic acids (Tables XVII and XX). On the other hand, if a second pair of hydrogen atoms is removed, with formation of a triple bond, the conductivity is considerably in-

42 Cf. p. 19.
43 Cf. p. 6.
44 The complete data for this acid will be published later.

creased. The values of μ_v for phenylpropiolic acid (Table V) are many times larger than the corresponding values for cinnamic. The same relation was found to exist in aqueous solution.[45]

Consider the following series—

Benzoic acid ..... C_6H_5COOH
m-Chlorbenzoic acid ..... $C_6H_4ClCOOH$
m-Nitrobenzoic acid ..... $C_6H_4NO_2COOH$
o-Toluic acid ..... $C_6H_4CH_3COOH$
p-Toluic acid ..... $C_6H_4CH_3COOH$

The conductivities of benzoic acid (Table I) and of o-toluic acid (Table XI) are about equal; whereas the conductivity of p-toluic acid (Table XII) is very much less. That the same relation holds also for other substituent groups may be seen from the results obtained last year by Wightman, Wiesel, and Jones.[46] For example, the conductivities of o-chlorbenzoic acid and of o-nitrobenzoic acid are approximately the same as that of benzoic acid; but the conductivities of the corresponding para-acids are considerably less.

It is a well-established fact that in aqueous solutions the conductivity of benzoic acid is somewhat increased by the introduction of a methyl, chlorine or nitro group in the para position, and enormously increased by the introduction of oue of these groups in the ortho position. In contradistinction to this, the effect of these groups upon the conductivity in alcoholic solution appears to be negative. Just the opposite is true if the chlorine or nitro group occupies the meta position, as can be seen from Tables XXIII and XXIV. In this case the conductivity of benzoic acid is somewhat increased.

Turn now to the following group—

Maleic acid .....

$$\begin{array}{l} H-C-COOH \\ \| \\ H-C-COOH \end{array}$$

Fumaric acid .....

$$\begin{array}{l} HOOC-C-H \\ \| \\ H-C-COOH \end{array}$$

Mesaconic acid .....

$$\begin{array}{l} HOOC-C-CH_3 \\ \| \\ H-C-COOH \end{array}$$

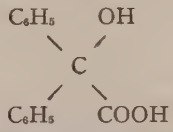
Itaconic acid .....

$$\begin{array}{l} CH_2 \\ \| \\ C-COOH \\ \| \\ CH_2-COOH \end{array}$$

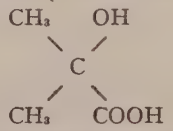
45 Cf. Carnegie Inst. Wash. Pub. No. 170, pp. 115 & 132.
46 Journ. Amer. Chem. Soc., 36. 2251-2 (1914).

The conductivity of maleic acid (Table VII) proves to be many times that of fumaric acid (Table VIII). This fact is in keeping with the results obtained in aqueous solution[47] and with the present day conception of the configuration of these acids. When one hydrogen atom in fumaric acid is replaced by a methyl group, the conductivity is increased slightly. Thus, the values of μ_v for mesaconic acid (Table VI) are uniformly higher than those of fumaric acid. Itaconic acid (Table IX), which has the same composition as mesaconic but differs in constitution, being methylene succinic acid, has a greater conductivity than mesaconic acid.

Benzilic acid, with the formula—



has a much greater conductivity than the corresponding methyl derivative, oxyisobutyric acid (Table XIV)—



This is in keeping with the results obtained for these acids in aqueous solution[48] and with the general observation that the replacement of a methyl group by a phenyl group increases the conductivity.

Esterification.

I have already called attention to the fact that the values of "per cent. decrease in normality," as given in Tables XXV to XLVIIII, are not thoroughly reliable. The reason for this will become apparent from the following considerations: Wightman, Weisel and Jones[49] found that when alcoholic solutions of the organic acids were titrated with aqueous ammonia, corallin being used as the indicator, a correction had to be made for the amount of ammonia necessary to produce color change. After this correction had been applied, the normality of any solution as determined with ammonia agreed to within 0.2 per cent. with that obtained by means of potassium hydroxide. In continuation of the investigation begun by Wightman, Wiesel and Jones, Mr. Wiesel and I have made a study of the conductivity and esterifi-

47 Carnegie Inst. Wash. Pub. No. 170. p. 113.
48 Carnegie Inst. Wash. Pub. No. 170, pp. 99, 110.
49 Journ. Amer. Chem. Soc., 36, 2250 (1914).

cation of alcoholic solutions of over forty organic acids. When we came to calculate from our data the values for "observed normality" and "per cent. decrease in normality," we found to our great surprise that except in the cases of the N/8 and N/512 solutions there were discrepancies in these values too great to be accounted for on the basis of experimental error. Because of this fact I have given the data in Tables XXV to XLVIII without any correction. They will, of course, be ultimately corrected.

An observation made by Goldschmidt in the course of his work on esterification has suggested to me a possible cause of these discrepancies. Goldschmidt found that when an alcoholic solution of an acid is titrated with an aqueous solution of a base, the end point as shown by the indicator depends upon the relative amounts of alcohol and water present. In other words, although the real neutral point cannot change, the point at which the solution is shown by the indicator to be neutral differs from the real neutral point by an amount which depends upon the ratio of alcohol to water present in the solution.

The bearing of this observation upon the point in question is at once apparent. The N/8, N/32 and N/128 solutions were titrated with ammonia of the same strength. The number of cubic centimeters of ammonia required were approximately 40, 10 and 2.5, respectively. Since 10 c. c. of the alcoholic solution were used in each titration, the ratios of alcohol to water were 4:16, 4:4 and 4:1, respectively. The effect of the alcohol would be hardly noticeable in the N/8 solution, both on account of the small proportion of it present and also because the solution is fairly concentrated. In the N/32 solution, however, the effect of the alcohol would be more marked, and in the N/128 solution still greater. Consequently the discrepancies would increase from N/8 to N/32 to N/128. Such is actually the case. The N/512 solution was titrated with a more dilute ammonia, and as about 25 c. c. were used, the same conditions prevailed as in the case of the N/8 solution No quantitative data are available by means of which I might apply corrections in accordance with these observations, and lack of time has prevented me thus far from undertaking to obtain such data experimentally. Therefore, it is with reluctance that I have recorded the esterification data without making corrections. In the near future, I hope to be able to return to the problem. I can, however, say with certainty that the extent to which the weaker organic acids undergo esterification under the conditions which prevailed during this investigation is extremely slight.

Johns Hopkins University,
Baltimore, Maryland,
May, 1915.

BIOGRAPHY

Howard Huntley Lloyd was born in Baltimore, Maryland, on August 1, 1892. He received his early education in the public schools and the City College of Baltimore. In the autumn of 1908 he entered the Johns Hopkins University as an undergraduate student, pursuing the chemical-biological course. From 1909 to 1912 he was the holder of Hopkins scholarships. In 1912 he was graduated, receiving the degree of Bachelor of Arts. After graduation he continued for three years the study of chemistry at the Johns Hopkins University. During the academic year 1912-1913 he held the position of laboratory assistant and during the following year that of lecture assistant, to Professor J. E. Gilpin. He was also a Hopkins scholar 1912-1913 and 1914-1915.